

Porous Poly(Vinylidene Fluoride) Membrane with Highly Hydrophobic Surface

Mao Peng,¹ Hongbing Li,² Lijuan Wu,¹ Qiang Zheng,¹ Ying Chen,¹ Wenfang Gu¹

¹Department of Polymer Science & Engineering, Zhejiang University, Hangzhou, 310027, China

²Saint-Gobain Ceramic Materials AS Shanghai, Shanghai, 200040, China

Received 18 November 2004; accepted 6 March 2005

DOI 10.1002/app.22303

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The preparation of very hydrophobic poly(vinylidene fluoride) (PVDF) membranes was explored by using two methods. The first one was the modified phase inversion method using a water/*N,N*-dimethylacetamide (DMAc) mixture instead of pure water as a soft precipitation bath. The second method was a precipitation-bath free method, that is, the PVDF/DMAc casting solution underwent gelation in the open air instead of being immersed into a precipitation bath. The morphology of the surface and cross section of the membranes was investigated by using scanning electron microscopy (SEM). It was found that the membranes exhibited certain micro- and nanoscale hierarchical roughness on the surface, which brought about an

enhanced hydrophobicity of the membrane. The contact angle (CA) of the samples obtained by the second method was as high as 150° with water. The conventional phase inversion method preparing PVDF porous membrane using pure water as precipitation bath usually results in an asymmetric membrane with a dense skin layer having a CA close to that of a smooth PVDF surface. The modified approach avoided the formation of a skin-layer and resulted in a porous and highly hydrophobic surface of PVDF. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1358–1363, 2005

Key words: contact angle; hydrophobic; phase inversion; PVDF

INTRODUCTION

Superhydrophobic solid surfaces having a contact angle (CA) with water larger than 150° have attracted a great interest in recent years, due to potential applications in industry and daily life. To date, many methods for the preparation of superhydrophobic surfaces have been reported in the literature, such as photolithography,¹ plasma fluorination,^{2,3} chemical vapor deposition,^{4,5} electrochemical deposition,⁶ chemical modification,⁷ and the preparation of aligned carbon nanotube forests^{8,9} or polymer nanofibers.¹⁰ However, it is difficult to prepare a large-area superhydrophobic surface using these methods, which obviously limits their applications. Recently, some attempts have been carried out by various researchers to prepare superhydrophobic surfaces using commercially available polymers and facile methods. For example, a superhydrophobic isotactic-polypropylene (i-PP) porous membrane with a CA of 160° with water was obtained by evaporation in vacuum from an i-PP solution of *p*-xylene/methyl ethyl ketone (MEK)¹¹; but, as mentioned by the author, there were obvious large cracks

on the surface of the superhydrophobic i-PP surface and they were not easy to avoid. Han and coworkers¹² introduced a pore structure to a Teflon membrane by stretching it at different extension ratios, and investigated its influence on the structure and CA. The maximum CA with water of the porous Teflon membrane was 160° when the extension ratio was 190%. Xu and Jiang et al.¹³ reported a facile one-step creation of a superamphiphobic coating by casting an *N,N'*-dimethylformamide (DMF) solution of PMMA and a fluorine-end-capped polyurethane (FPU); the maximum CA with water was reported as 166°.

PVDF is a commercially available fluoropolymer with low surface energy and good physical, chemical, and mechanical properties. Also, being an engineering thermoplastic, PVDF has better stiffness and strength than those of most fluorine-containing polymers. And because of its exceptional chemical stability and excellent resistance to aging, PVDF has been widely used in industry. For example, the history of PVDF being used as a long-term architectural coating can be traced for more than 30 years, and it has exhibited excellent durability.¹⁴ In addition, PVDF can be made into a porous membrane on a large scale in industry. Some kind of microporous PVDF membrane prepared by the phase inversion method has been used for lithium-ion batteries, pervaporation or film filtration, protein purification, bacteria filtration, water purification, gas separation, and so forth.^{15–19}

Correspondence to: M. Peng (pengmao@zju.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; Contract grant number: 50203013.

Obviously, superhydrophobic surfaces reported in the literature are made from materials combining both hydrophobicity and surface roughness. Therefore, it is reasonable for one to expect that PVDF membrane with a porous surface structure should have enhanced hydrophobicity. Being a fluoropolymer, PVDF has low surface energy (25 dynes/cm) compared with polypropylene (29–31 dynes/cm) that contains only C-H and C-C bonds, but it has highly dipolar molecules for being only partially fluorinated; therefore, it is intrinsically polar, with lower CA with water compared with that of PP (92–104°). This is also the precondition for PVDF being used in piezo- and pyroelectric materials, when the correct morphology is achieved. Generally, a superhydrophobic surface is made by introducing roughness to a hydrophobic surface with a contact angle larger than 90°. Jiang and coworkers¹⁰ found that poly(vinyl alcohol) (PVA) nanofiber forest can be superhydrophobic, although PVA is an amphiphilic polymer with a static CA of $72.1 \pm 1.1^\circ$ with water. Therefore, an interesting postulate can be inferred from the above scenario, that is, how hydrophobic can PVDF membrane be after its surface roughness is increased?

Cheng and colleagues^{20–22} systematically investigated the phase structure of PVDF porous membrane obtained from the phase inversion method; but, as far as we know, no attention has been paid to the surface properties of the membrane to date. In this study, we modified the conventional phase inversion method, preventing the formation of a dense skin layer on the surface of PVDF membrane, and the resultant PVDF membrane had a porous surface and near superhydrophobicity, with an average CA of 146° and maximum CA of 151° with water. The relationships between surface morphology, hydrophobicity, and preparation methods were investigated in detail.

EXPERIMENTAL

Materials

PVDF (with number-average molecular weight of 165,850, weight-average molecular weight of 331,352, polydispersity index of 1.99, and melting point of 172°C) was obtained in a pellet form from Zhejiang Chemical Industrial Institute, Shanghai, China. *N,N*-dimethylacetamide (DMAc) and ethanol (both reagent grade) were purchased from the China Medicine (Group) Shanghai Chemical Reagent Corp., Shanghai, China. All chemicals and materials were used as received.

Membrane preparation

20 g PVDF granules were put in 80 g DMAc in a triangle beaker, and the mixture was agitated for sev-

eral hours at 70°C on a magnetic heating stirrer until the solution was homogeneous and clear. Porous PVDF membranes were prepared by the following three methods, respectively.

The first is the conventional phase inversion or immersion-precipitation method, in which the PVDF/DMAc solution was spread uniformly on the surface of a poly(ethylene terephthalate) (PET) sheet. The solution-casting film was then immersed immediately in water, the precipitation bath, or in other words, the coagulation bath, since water is the nonsolvent for PVDF. The PVDF membrane turned opaque soon after contact with water, indicating the coagulation and precipitation of PVDF from the solution, finally forming a translucent, white, flat membrane. Then, the wet membrane was soaked in ethanol several times to completely remove residual DMAc and water. The membrane was then dried in open air and then in a heated vacuum oven at 60°C.

As will be discussed in detail in the following part, the PVDF membrane obtained in the above experiment had an asymmetric structure with a dense skin layer. The surface of the membrane had a hydrophobicity close to that of a smooth PVDF surface. Therefore, in the second method, a relatively soft coagulation bath, employing a mixture of water and DMAc at different ratios, was used instead of water to prevent the formation of a dense skin layer. The ratio of water to DMAc was 75 : 25, 50 : 50, 35 : 65, and 25 : 75, respectively.

In the third experiment, to further simplify the preparation, a gelation-in-air method was used instead of the immersion-precipitation method in the conventional phase inversion technique. The PVDF casting solution was placed in the open air until gelation occurred. Instead of being immersed in water or some other precipitation bath, the gel film of the PVDF/DMAc casting solution, which was still optically clear, was soaked directly in ethanol several times to remove residual DMAc. Then, the wet membranes were dried in the open air or in a vacuum oven at 60°C.

Characterization of morphology and static contact angle

The morphology of the top surface (defined as the surface contacting with the precipitation bath or the nonsolvent), the bottom surface (the surface contacting with the PET sheet substrate), and the cross section of the sample films was characterized by using SEM (JSM-5510LV, JEOL, Japan) operated at 20 kV. Before experiments, all the samples were coated with gold in vacuum for observation.

The static contact angle of the PVDF membrane was measured by the sessile drop method with a contact angle meter (DSA10-MK2, Krüss, Germany). The water droplet used for measurement was 8 μ L. The con-

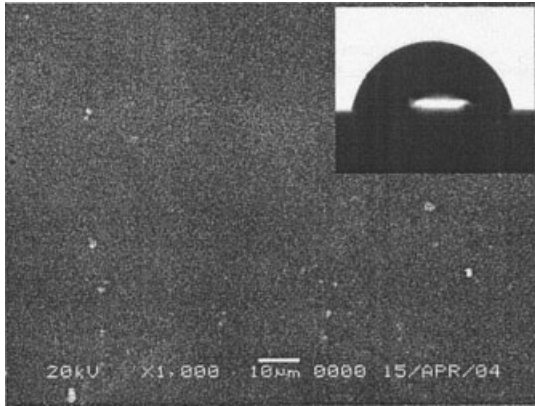


Figure 1 The SEM image of the smooth surface of the PVDF membrane obtained by hot-pressing. The insert is the profile of a water droplet on the surface with a CA of $82.0 \pm 0.5^\circ$.

tact angle values of each sample were measured at five various positions of one sample and then averaged.

RESULTS AND DISCUSSION

Figure 1 presents a SEM photograph of the surface of the smooth and dense PVDF membrane obtained by hot pressing and then cooling in the air. The insert in

Figure 1 presents the profile of a water droplet on the surface of a smooth PVDF membrane with a contact angle of $82.0 \pm 0.5^\circ$.

Figures 2(a) and (b) present the morphology of the top surface (the surface in contact with the precipitation bath water) and the bottom surface of the PVDF membrane obtained by the phase inversion method with pure deionized water as the precipitation bath. Obviously, the top surface is nearly smooth, with no observable porous structure even when the magnification is 5000. On the contrary, the bottom surface of the PVDF membrane is obviously porous, with interconnected holes in the networks constructed by PVDF small spheres connecting with each other. The inserts in Figures 2(a) and (b) present a profile of the water droplet on the top and bottom surface of the PVDF membrane just mentioned. The CA with water in Figures 2(a) and (b) is $85.2 \pm 3.2^\circ$ and $142.6 \pm 1.3^\circ$, respectively. Obviously the smooth top surface has a CA very close to the smooth PVDF surface obtained by hot-pressing in Figure 1.

The morphology of the cross section of the PVDF membrane exhibits an obvious asymmetric structure, as is shown in Figures 2(c) and (d). Obviously, there is a dense skin layer on the top surface that is in direct contact with water, in the precipitation bath. This is consistent with Figure 2(a), the vertical view of the top

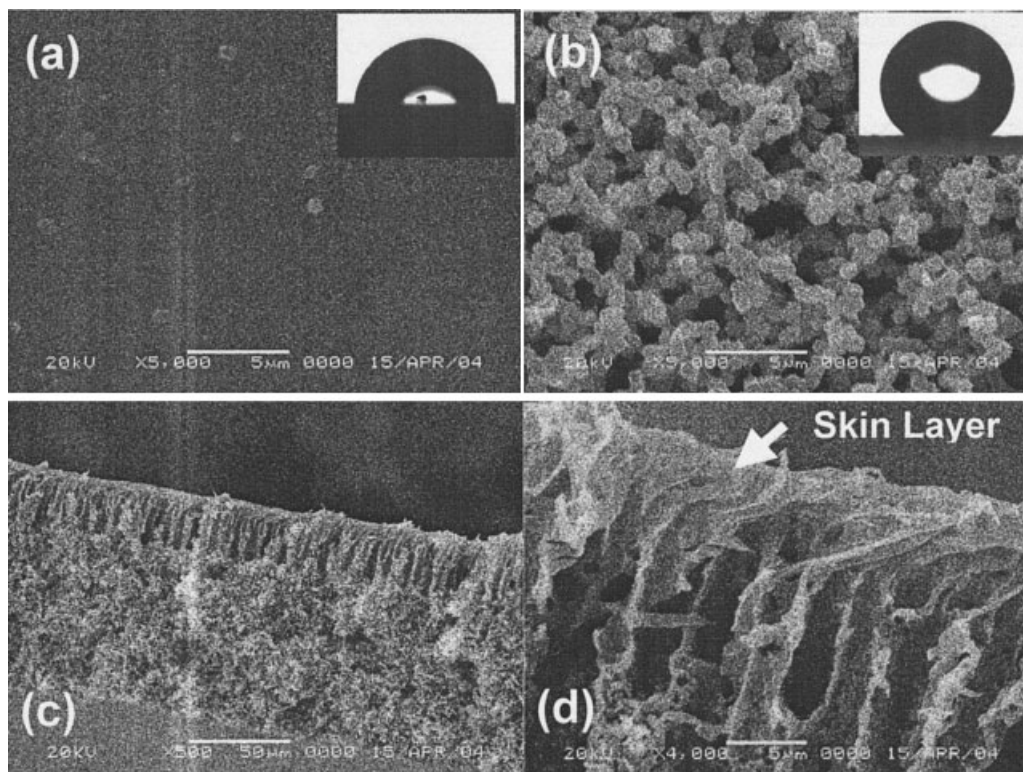


Figure 2 SEM images of: (a) the top surface of the PVDF membrane obtained by the phase inversion method, (b) the bottom side of the membrane, (c) the cross section of the membrane with magnification of 500, (d) the cross section with magnification of 4000. The inserts in (a) and (b) are the profile of a water droplet on the top and bottom surface, respectively.

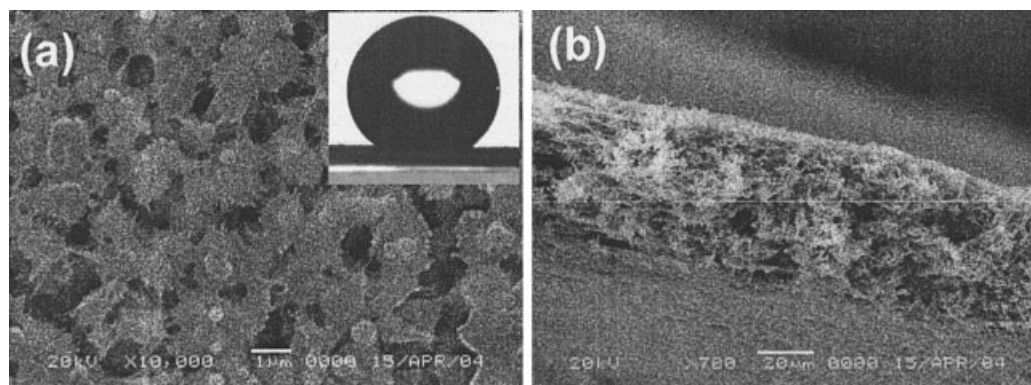


Figure 3 SEM images of: (a) the top surface of the PVDF membrane obtained by phase inversion in a soft precipitation bath with water/DMAc ratio of 35 : 65. (b) The cross section of the membrane. The insert in (a) is the profile of a water droplet on the top surface.

surface. An anisotropic porous layer of about 20 μm with columned large pores is beneath the skin layer. The major axis of the pores is perpendicular to the surface. The major part of the membrane has an isotropic pore structure beneath the anisotropic porous layer and skin layer. As can be observed in Figure 2(b), a large amount of small spheres with average diameter of about 1 μm adhering to each other form a sponge-like porous structure. This explains the highly hydrophobic property of the bottom surface of the PVDF membrane. The asymmetric structure results from the complicated mass transfer of nonsolvent, liquid-liquid phase separation, and crystallization behavior of PVDF during the immersion-precipitation process, as have been reported by Cheng and coworkers.^{20–22} It is important to the preparation of an asymmetric membrane used for film filtration, but unfortunately the asymmetric structure with a dense skin layer is fatal for obtaining a highly hydrophobic PVDF surface; therefore, it should be avoided. However, the fact that the bottom surface of the PVDF membrane exhibits high hydrophobicity confirms the expectation that increased roughness helps to enhance hydrophobicity for PVDF, even though it has intrinsically polar molecules.

To prepare a PVDF membrane with a porous surface, the phase inversion process was carried out in a soft coagulation bath, a mixture of water and DMAc, with the ratio (water to DMAc by weight) of 75 : 25, 50

: 50, 35 : 65, and 25 : 75, respectively. The membranes were soaked in ethanol and dried.

The insert in Figure 3(a) presents the typical profile of a water droplet on the top surface of a PVDF membrane obtained by phase inversion using water/DMAc (35 : 65) as the soft precipitation bath. It was found that the hydrophobicity of the top surface and the bottom surface are both larger than 140°, indicating that the soft precipitation bath prevented the formation of an asymmetric structure in the PVDF membrane. Figures 3(a) and (b) present the SEM photographs for the surface and cross-sectional morphology of the PVDF membrane obtained by using a water/DMAc mixture (35 : 65) soft precipitation bath. It is obvious that the membrane exhibits an isotropic sponge-like structure, with both top and bottom porous surfaces. The CA of the two sides of the membrane has no important differences. Table I summarizes the CAs for the top and bottom surfaces of PVDF membranes obtained in different precipitation baths. It was found that asymmetric membranes were obtained for mixtures with water content higher than 50 wt %. For water content less than 50 wt %, a high hydrophobic top surface of the PVDF membrane can be obtained. This indicates that the casting PVDF solution in the soft precipitation bath, with DMAc content larger than 50 wt %, undergoes phase separation and crystallization in a relatively uniform way, so a symmetric structure forms. However, the disadvan-

TABLE I
Contact Angles for the Top and Bottom Sides of PVDF Membranes Obtained by the Phase-Inversion Method Using a Soft Precipitation Bath with Various Water/DMAc Ratios

Position on the sample	Contact angles for various water/DMAc ratios				
	100 : 0	75 : 25	50 : 50	35 : 65	25 : 75
Top side	85.2 \pm 3.2°	114.0 \pm 3.2°	130.4 \pm 3.7°	141.5 \pm 4.2°	139.5 \pm 3.9°
Bottom side	142.6 \pm 1.3°	144.7 \pm 2.0°	140.2 \pm 3.0°	143.1 \pm 2.4°	141.0 \pm 5.4°

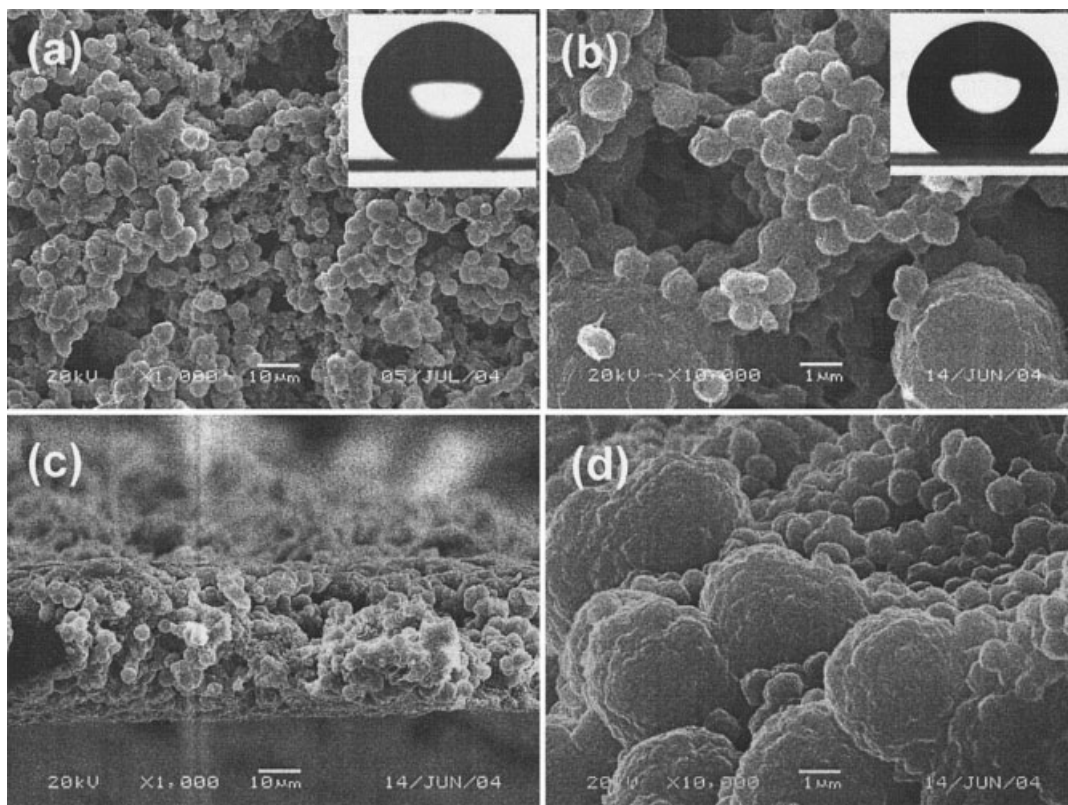


Figure 4 SEM images of: (a) the top surface of the PVDF membrane obtained by the gelation-in-the-air method, (b) the bottom side of the membrane, (c) the cross section of the membrane with magnification of 1000, (d) the cross section with magnification of 4000. The inserts in (a) and (b) are the profile of a water droplet on the top and bottom surface, respectively.

tage of this method was that a large amount of organic DMAc solvent was employed in the precipitation bath. Furthermore, the PVDF casting solution swelled in the precipitation bath, resulting in a mechanically very weak gel that easily deformed, distorted, or peeled in the experiment. With the increase of DMAc content, the swelling of PVDF/DMAc casting solution turned out to be more serious. In fact, the membranes with high hydrophobicity had poor surface uniformity. Therefore, the method needed further modifications.

As was mentioned in the Experimental section, in the third experiment, the PVDF porous membrane was obtained by using the gelation-in-the-air method, instead of coagulating in a precipitation bath as in conventional phase inversion methods. The lack of coagulation bath leads to a more environmentally friendly and easier preparation. PVDF membranes obtained in this way are flat and uniform, having good appearance and mechanical strength. The profile of a water droplet on the top surface of a PVDF membrane is presented in the insert of Figure 4. It has a CA as high as $150.6 \pm 0.4^\circ$, which is superhydrophobic. There is no difference between the top and the bottom surfaces. But, unfortunately, most samples obtained in the same way have CAs ranging from 144 to 149° , which is not superhydrophobic. How-

ever, it can be confirmed that the hydrophobicity of PVDF can be dramatically improved by introducing a porous structure to its surface.

Figures 4(a), (b), and (c) present the SEM pictures of the surface, bottom, and cross-sectional morphology of the PVDF membrane obtained by the gelation-in-air method. The membrane has a symmetric structure. In addition, the membrane exhibits a micro- and nanoscale hierarchical structure. There are large crystalline spheres of PVDF with a diameter of about $4 \mu\text{m}$, and a large amount of smaller spheres with a diameter less than $1 \mu\text{m}$. Enlarged photos [Fig. 4(d)] indicate that the large spheres have no smooth surface; on the contrary, their surface has a large amount of hemispherical papillae with a size of several hundred nanometers. We believe that this hierarchical structure results from liquid-liquid phase separation and the crystallization process during gelation and ethanol soaking. But, obviously, much work needs to be done in the future to illuminate the mechanism for the formation of this structure. According to Jiang and colleagues,¹⁰ the macro- and nanoscale hierarchical structure play important roles in the superhydrophobicity of lotus. Therefore, it is also responsible for the greatly improved hydrophobicity of the PVDF porous membrane obtained by the gelation-in-air method.

The limitation of PVDF microporous membrane is its relatively low hydrophobicity compared with other superhydrophobic polymers reported in the literature. Some samples have CA less than 150° . This results from the intrinsic polarity of the PVDF molecular structure. However, compared with superhydrophobic Teflon¹² and polypropylene as was widely reported in the literature,^{3,11} PVDF combines good processability, mechanical properties, chemical stability, durability, and heat resistance. It is also reasonable to believe that our method can be used to prepare large-area PVDF coatings or membranes with enhanced hydrophobicity on a large scale, because the preparation of porous asymmetric PVDF membranes has been successfully industrialized for many years. In addition, all the procedures can be carried out at ambient temperature and no vacuum drying is necessary. Therefore, we believe that the highly hydrophobic PVDF membrane reported in this paper can find applications in some appropriate areas in the future.

CONCLUSIONS

In this study, we found that a symmetric porous PVDF membrane can be obtained by using a modified phase inversion method using a soft precipitation bath of water/DMAc mixture with a water/DMAc ratio smaller than 50 : 50, and by using a gelation-in-the-air method instead of the immersion-precipitation phase inversion method. The asymmetric structure and dense skin layer formed during the phase inversion process using pure water as a precipitation bath was completely prevented. The top surface of the sponge-like porous PVDF membrane exhibited greatly enhanced hydrophobicity, having a CA from 140° to 151° with water. This provides a novel and facile but effective method to prepare a highly hydrophobic surface based on PVDF, a fluoropolymer with excellent comprehensive properties.

References

1. McCarthy, T. J.; Oner, D. *Langmuir* 2000, 16, 7777.
2. Woodward, I.; Schofield, W. C. E.; Roucoules, V.; Badyal, J. P. S.; *Langmuir* 2003, 19, 3432.
3. Youngblood, J. P.; McCarthy, T. J. *Macromolecule* 1999, 32, 6800.
4. Liu, H.; Feng, L.; Zhai, J.; Jiang, L.; Zhu, D. *Langmuir* 2004, 20, 5659.
5. Teshima, K.; Sugimura, H.; Inoue, Y.; Takai, O.; Takano, A. *Langmuir* 2003, 19, 10624.
6. Li, M.; Zhai, J.; Liu, H.; Song, Y.; Jiang, L.; Zhu, D. *J Phys Chem B* 2003, 107, 9954.
7. Granville, A. M.; Brittain, W. J. *Macromol Rapid Commun* 2004, 25, 1298.
8. Sun, T.; Wang, G.; Liu, H.; Feng, L.; Jiang, L.; Zhu, D.; *J Am Chem Soc* 2003, 125, 14996.
9. Lau, K. K. S.; Bico, J.; Teo, K. B. K.; Chhowalla, M.; Amaratunga, G. A.; Milne, W. I.; McKinley, G. H.; Gleason, K. K. *Nano Lett* 2003, 3, 1701.
10. Feng, L.; Song, Y.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2003, 42, 800.
11. Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* 2003, 299, 1377.
12. Zhang, J.; Li, J.; Han, Y. *Macromol Rapid Commun* 2004, 25, 1105.
13. Xie, Q.; Xu, J.; Feng, L.; Jiang, L.; Tang, W.; Luo, X.; Han, C. C. *Adv Mater* 2004, 4, 302.
14. Wood, K. A.; Cypcar, C.; Hedhli, L. *J Fluorine Chem* 2000, 104, 63.
15. Saunier, J.; Alloin, F.; Sanchez, J. Y.; Barrière, B. *J Polym Sci Part B: Polym Phys* 2004, 42, 532.
16. Lin, D.; Chang, C.; Shaw, H.; Jeng, Y.; Cheng, L. *J Appl Polym Sci* 2004, 93, 2266.
17. Roy, C. C.; Chowdhury, G.; Matsuura, T. *J Appl Polym Sci* 1997, 65, 1263.
18. Oshima, K. H.; Evans-Strickfaden, T. T.; Highsmith, A. K.; Ades, E. W. *Biologicals* 1996, 24, 137.
19. Charcosset, C. *J Chem Technol Biotechnol* 1998, 71, 95.
20. Lin, D.; Beltsios, K.; Chang, C.; Cheng, L. *J Polym Sci Part B: Polym Phys* 2003, 41, 1578.
21. Lin, D.; Chang, C.; Chang, C.; Chen, T.; Cheng, L. *J Polym Sci Part B: Polym Phys* 2004, 42, 830.
22. Cheng, L.; Lin, D.; Shih, C.; Dwan, A.; Gryte, C. C. *J Polym Sci Part B: Polym Phys* 1999, 37, 2079.